

## EXTRACTION AND DESULFURIZATION OF CHEMICALLY DEGRADED COAL WITH SUPERCRITICAL FLUIDS

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### INTRODUCTION

In the systematic investigation of "Extraction and Desulfurization of Coal With Supercritical Fluids", it was found that sulfur materials in coal were removed selectively from the coal matrix, employing ethanol or methanol as the solvent. It is a well-known fact that a fluid under supercritical conditions exhibits an enhanced dissolution power which can increase the solubilities of various organic materials by several hundredfold. Depending upon the specific compounds and the solvent involved, solubility of each organic compound in a given solvent may vary at different temperatures and pressures. This differentiation of solubilities will allow selective removal of certain organic matter under supercritical conditions.

When ethanol or methanol is used as supercritical fluid, chemical reactions may be taking place between sulfur compounds in coal and the solvent in the presence of mineral matter. Pyritic sulfur may be reduced, and certain organic sulfur materials may be removed through chemical reactions. In this situation, the reactivity between organic sulfur in coal and supercritical alcohols is not only dependent on reaction conditions, but is also dependent on the distribution of sulfur functional groups in coal. That is to say, some forms of sulfur compounds are easier to be reacted and subsequently extracted than others. Therefore, the desulfurization potential with supercritical fluids may be affected by the coal types and sources, since various coals may have different sulfur functional groups in their respective structures.

In order to better understand the complex system of desulfurization of coal with supercritical alcohols, we have launched an extensive experimental study to achieve the following research objectives. They are: (1) to determine the selectivity of desulfurization of coal with supercritical alcohols, (2) to determine the effect of chemical pre-treatment on supercritical desulfurization potential, (3) to evaluate the gaseous and liquid product streams, and to characterize the desulfurized solid char for establishing the material and sulfur balances, and (4) to evaluate the physical and chemical transformation of coal during supercritical desulfurization.

### LITERATURE REVIEW

Most work on supercritical extraction of coal reported in the literature has as a primary objective the maximum conversion of coal to liquid products. A 1975 article by Whitehead (9) [one of the first references to supercritical

coal extraction presented in the literature] presented data on supercritical extraction of coal by coal tar or petroleum naphtha fractions. Tugrul and Olcay (8) reported in 1978 extractions yields and analytical results obtained by supercritical-gas extraction of 250 mesh lignite. They found extraction nearly complete after 30 minutes; extract yields of about 24% were reported. Gas chromatography/mass spectrometry analyses of several extract fractions indicated dozens of paraffins, alkylated hydrocarbons, phenolic and oxygenated compounds; however, no sulfur compounds were reported. A kinetic study of a high-volatile bituminous coal utilizing supercritical toluene was reported by Slomka and Rutkowski (7). A close fit of their experimental data on time dependence of extraction yield was found when a second order equation was used. The use of supercritical toluene extraction of coal in pilot plant studies supported by the British Coal Board was reported by Maddocks (3). The major objective of that study was also maximum conversion of coal to liquid products; reduction of sulfur in the unconverted solid was not reported.

Some work has been reported utilizing alcohols for supercritical extraction of coal. Makabe, et al. (4) reported extraction of coal with ethanol-sodium hydroxide with the objective of maximizing extraction yield; no sulfur data was reported. Methanol reaction with a low volatile Bituminous West Virginia coal at higher temperatures (460 - 600°C) was reported by Garner, et al. (2). Promotion of coal gasification was the objective of that study; sulfur content of the resultant char was not reported.

In contrast to the previous reported work utilizing supercritical solvent extraction of coal, where major objectives have been the conversion of coal to liquid or gaseous products, the major objective of our research effort is to study supercritical desulfurization of coal with alcohols. Researchers at Purdue University have studied the supercritical desulfurization of coal by using water as a solvent. Although their data have indicated that pyritic sulfur was effectively removed, the rate of removal of organic sulfur was found to be very slow.

The recent article by Amestica and Wolf (1) does compare results obtained with toluene and ethanol when used for the supercritical extraction of an Illinois No. 6 coal. The experimental apparatus employed appears similar to ours, and temperatures utilized for the ethanol extraction (350 - 450°C) are also comparable. The ethanol/coal ratio of 7/1 is greater than the 1/1 ratio that we normally utilize in the batch reactor system, and the reaction time of 30 minutes is less than the 1 or 2 hour reaction periods we normally employ.

In the article, it is reported that the "sulfur rejected" varied from 1.7% to 11.7% in the three runs reported. However, a footnote given in the table states these values were calculated as a "sulfur percentage of daf coal feed in the gas phase". The text indicates determination of the sulfur was accomplished by scrubbing of the uncondensed gases in a zinc acetate solution. No data are given in the article with respect to the sulfur content of the solid product, nor is mention made of sulfur analyses on the liquid product. To interpret the sulfur captured from the uncondensed gases by a zinc acetate solution as being a measure of the "sulfur rejected" from the coal during the supercritical extraction implies that all the sulfur removed was accounted for; this seems to be a risky assumption, based on the lack of appropriate data presented in the article.

The possibility of condensation reaction of solvent degradation products occurring during supercritical extraction of coal with ethanol and alkali-ethanol is supported by data given by Makabe and Ouchi (5, 6). However, as the discussion that follows will indicate, we have not found evidence that this occurs under the conditions we employ for supercritical desulfurization of coal with alcohols.

## EXPERIMENTAL

Most of the investigation was performed in two reactor systems. They are a semi-continuous reactor and a batch reactor. Their respective experimental set-ups are described in the following.

### Semi-Continuous Reactor Studies

The flow chart for the semi-continuous Berty gradientless reactor, equipped with a Magne-drive impeller and internal recirculation systems, is given in Figure 1. The ground coal is held in a basket within the reactor, while solvent is pumped continuously through the system. After cooling following a run, the solid product is removed from the reactor basket for weighing and analysis. It is possible to maintain a constant pressure in this system, in contrast to the batch system where pressure increases during the course of a run, final pressure being determined by the temperature and charge size of the reactor.

### Batch Reactor Studies

Figure 2 shows the flow diagram of the 300 cc batch reactor system that has been utilized in our experiments. The coal and solvent are charged to the reactor, heated to reaction temperature, and maintained at reaction temperature for a designated period; generally one or two hours. After reaction, the separation of products is accomplished by venting the fluid phase slowly from the reactor through the product collection system.

As shown in Figure 1, the product collection system consists of a water cooled condenser and primary liquid collection vessel, followed by a dry ice-acetone cooled cold trap coil and a series of three absorption vessels. The non-condensable gases are then discharged through a sample vessel and to a wet test meter for volume measurement. The first two absorbers contain ethyl alcohol; the third absorber contains an aqueous zinc acetate solution.

The total sulfur measurements were performed on a Fisher Total Sulfur Analyzer. The starting coal, the solid product resulting from the supercritical desulfurization reaction, the primary liquid product collected, additional liquid recovered from the cold trap (if any), and samples from each of the absorbers were analyzed.

## RESULTS AND DISCUSSIONS

### Semi-Continuous Reactor Results

Figures 3 and 4 show the data of sulfur removal and coal extraction for four different coal samples with supercritical ethanol at 325°C and 1750 psi. It can be seen that the percent of sulfur removed is much higher than the

percent coal extracted (weight loss of coal). A term called desulfurization selectivity ratio which is defined as the ratio of percent of sulfur removed to percent of coal extracted, varied between 2.96 to 4.38 under these conditions as shown in Table 1.

TABLE 1  
SUPERCRITICAL ETHANOL DESULFURIZATION OF COAL  
AT 325°C; 1750 psi  
Desulfurization Selectivity Ratio

Extraction Time, Hours	Desulfurization Selectivity Ratio			
	Coal "A"	Coal "B"	Coal "C"	Coal "D"
0	2.81	3.40	4.09	12.0
1	3.29	2.98	3.40	7.36
2	3.81	2.88	3.10	5.49
4	3.39	2.96	3.49	4.38

A series of experiments were performed to evaluate whether or not a pre-treatment of coal with KOH solution will enhance the desulfurization efficiency. In the pre-treatment, 60 grams of coal particles were soaked in 180 grams of KOH in ethanol solution with a given concentration for five minutes, filtered, washed twice with 180 grams of ethanol and filtered again before its use. The results are presented in the following.

TABLE 2  
THE EFFECT OF KOH PRE-TREATMENT  
(275°C and 1800 psia)

	<u>% of Sulfur Concentration Removed</u>
No pretreatment	21.3
2% KOH	28.5
3% KOH	28.9
4% KOH	29.8
5% KOH	34.0

The data indicates that an improvement of desulfurization potential was realized with KOH pre-treatment.

In order to evaluate the degree of potassium ion incorporation into the coal structure during the pre-treatment, several experiments were conducted at 325°C and 1750 psia employing ethanol or methanol as solvent. In these experi-

ments, the soaking and washing solutions were collected, and were analyzed for potassium ion on a Perkin Elmer Atomic Adsorption Spectrometer. It can be seen in Table 3 that most of the potassium ion was found in the solution.

TABLE 3  
POTASSIUM ION BALANCE

KOH Pre-treatment	Ethanol		Methanol	
	% S Removed	% K <sup>+</sup> Recovered	% S Removed	% K <sup>+</sup> Recovered
None	27.0	--	30.2	--
5% KOH, soaking, rinsing	32.16*	102	39.1	99

\*Average of three experiments

#### Batch Reactor Results

Table 4 shows a summary of experimental data (elemental analysis) of the desulfurized coal samples for the batch reactor system under different operating conditions. The original coal has a total sulfur content of 4.27 percent, and 72.6 percent of the total sulfur is organic sulfur. Since the concentration of total sulfur in the solid product from the supercritical desulfurization is reduced nearly 50 percent or more for five out of nine cases, and the sulfur removals resulting from the supercritical desulfurization exceeds the pyritic sulfur content of the original coal, it is concluded that organic sulfur in this coal is being removed. The possibility that the selective removal of sulfur may be due to condensation reactions of the solvent, with subsequent incorporation in the coal matrix, may also be rejected by consideration of H/C ratio data in Table 4. If significant incorporation of  $-CH_2-$  groups from the solvent were to occur, an increase in H/C ratio would be expected. As the data indicated, the H/C ratio actually decreases during the supercritical desulfurization.

Table 5 summarizes the sulfur balance information obtained on a series of batch reactor runs under a variety of conditions. Note that the sulfur determined in the liquid products and in the absorber total from 67.1% to 94.7% of the total sulfur removed from the coal during the supercritical desulfurization. When the sulfur content of the solid product is included, the overall sulfur balance ranges from 82.4% to 97.1% of the sulfur contained in the original coal.

The total materials balance of these experiments ranges between 92.4% to 100.6%.

#### CONCLUSIONS

It is concluded from experimental information obtained that sulfur, including organic sulfur in coal, is selectively recovered from coal matrix with supercritical alcohol. The effect of chemical pre-treatment with KOH soaking

and/or acid leaching is found to be significant. The pre-treatment step may help the depolymerization of coal structure which makes it easier for super-critical alcohol to reach the sites of sulfur compounds for extraction and conversion.

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TABLE 4  
ELEMENTAL ANALYSES OF SOLID PRODUCT FOR BATCH REACTOR SYSTEM

Solvent and Conditions <sup>a</sup>	C	H	N	S	H/C Ratio	% S Removed (Conc. Based)
Original raw coal	66.04	4.85	1.17	4.27	0.881	
MeOH	72.63	4.04	1.31	2.99	0.667	30.0
MeOH + 5% KOH	70.37	3.72	1.25	1.96	0.634	54.1
HCl refluxed; MeOH	77.17	3.05	1.32	2.16	0.474	49.4
MeOH + 5% KOH + CO 400 psi	69.60	4.15	1.18	2.58	0.716	39.6
Acid leached <sup>b</sup> ; MeOH + 5% KOH	71.91	3.96	1.23	1.53	0.661	64.2
Acid leached <sup>c</sup> ; MeOH + 5% KOH	73.32	3.07	1.30	1.88	0.502	56.0
MeOH + 5% KOH; Two stage	69.16	3.18	1.12	1.47	0.552	65.6
EtOH	75.82	3.95	1.39	2.75	0.625	35.6
EtOH + 5% KOH	73.90	3.32	1.24	2.60	0.539	39.1

<sup>a</sup>All run at 350°C

<sup>b</sup>Soaked for 48 hours

<sup>c</sup>Soaked for 4 hours

TABLE 5  
SULFUR BALANCE

Solvent	Rxn T C	% Reductn of Sulfur in Coal	% of Sulfur Removed as Found in			Overall Sulfur Balance
			Liq.	Absorber	Total	
EtOH	350	31.4	43.3	43.7	87.0	93.9
EtOH	375	36.8	13.2	81.5	94.7	97.1
MeOH + 5% KOH	350	53.9	12.4	64.3	76.7	85.7
MeOH + 5% KOH	350	56.1	7.2	74.0	81.2	88.2
MeOH	350	48.8	6.9	60.2	67.1	82.4

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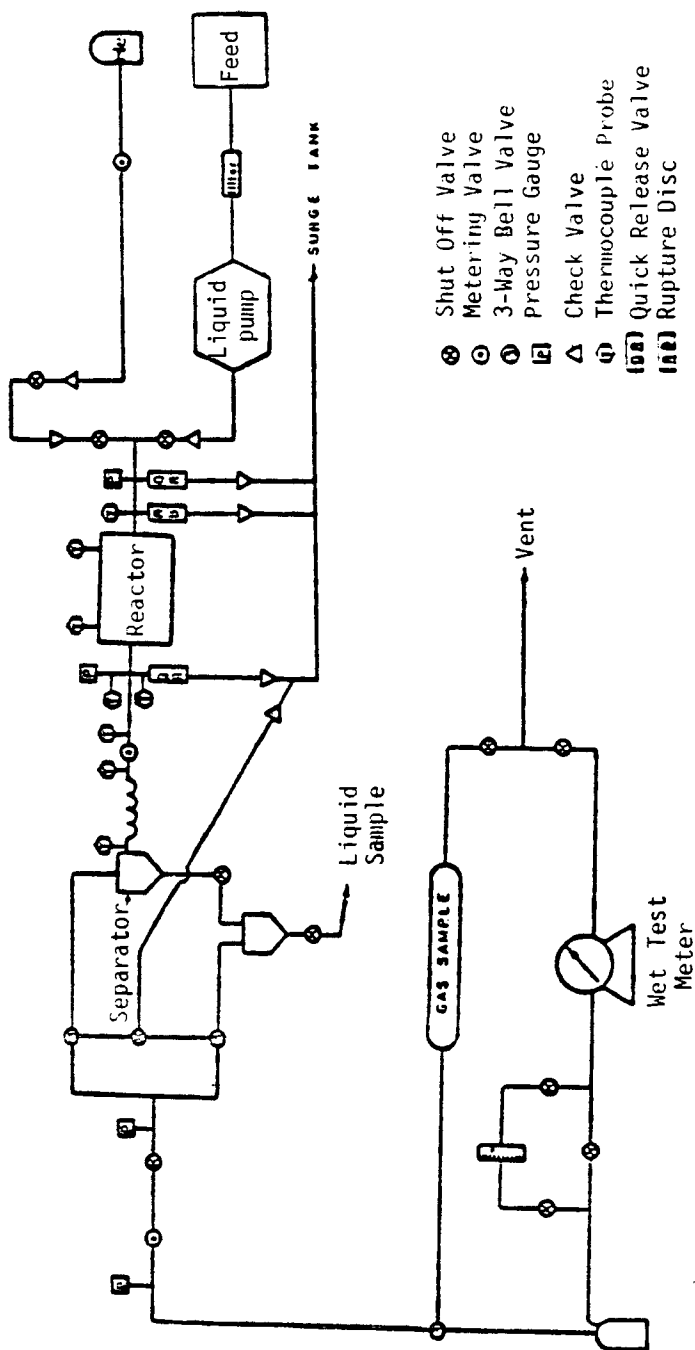


Figure 1. Flow Diagram of the Experimental Setup  
Semi-Continuous Reactor



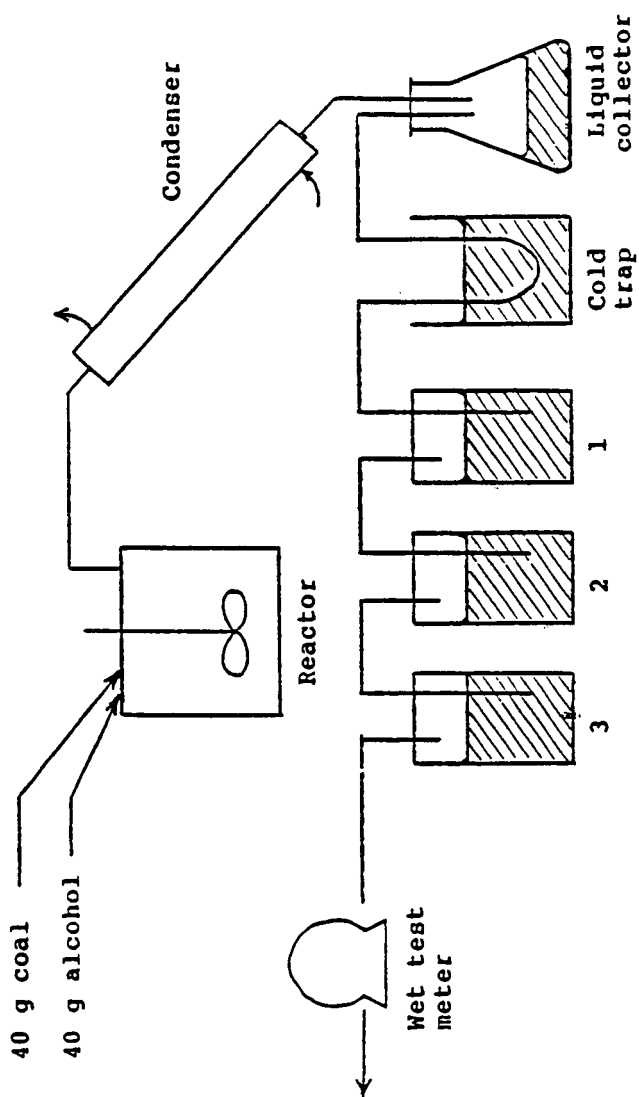


Figure 2. Batch Reactor Flow Diagram  
Absorbers 1 and 2 contain ethanol, 3 contains aqueous zinc acetate solution.

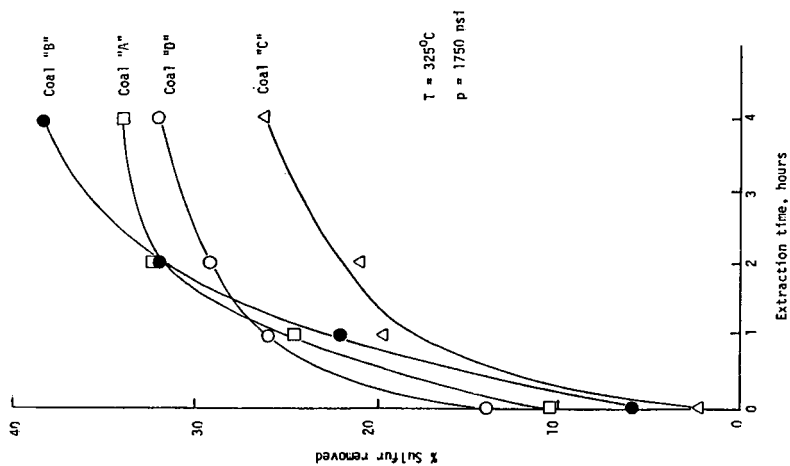


Figure 4. Percent of Sulfur Removed in Semi-Continuous Reactor

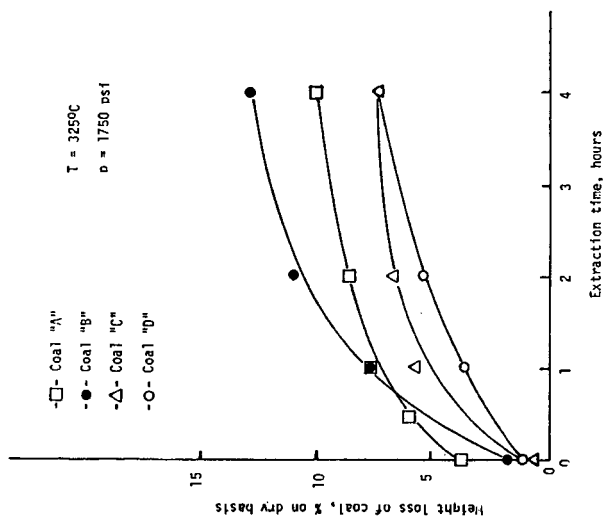


Figure 3. Percent of Coal Extracted in Semi-Continuous Reactor